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(11)

EP 0 835 684 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
15.04.1998 Bulletin 1998/16

(51) Int Cl.⁶: **B01D 53/94**(21) Application number: **97307691.2**(22) Date of filing: **30.09.1997**

(84) Designated Contracting States:
**AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC
NL PT SE**
Designated Extension States:
AL LT LV RO SI

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(30) Priority: 11.10.1996 GB 9621215

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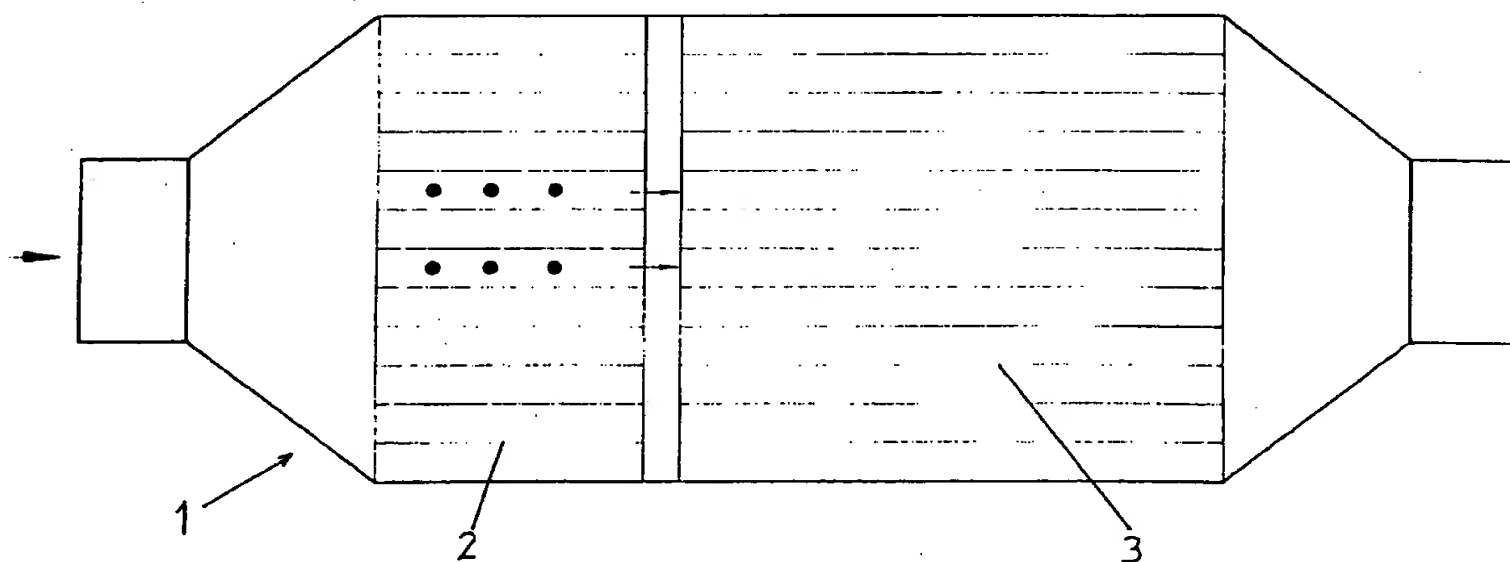
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(54) Emission control

(57) An emission control system especially for light duty diesel engines has a first catalyst, 2, positioned upstream of a second catalyst, 3. The first catalyst con-

verts NO to NO₂ and the second catalyst oxidises HC, NO and VOF. The tendency of the second catalyst to collect soot particles is reduced by combustion of the soot particles by NO₂ from the first catalyst.



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Description

The present invention concerns emission control, and more especially it concerns the reduction or elimination of soot particle emission from internal combustion engine exhaust gas, particularly that from diesel (compression ignition) engines.

Although diesel engines generally emit considerably less gaseous pollutants, *ie* hydrocarbons ("HC"), carbon monoxide ("CO") and volatile organic fractions ("VOF") than gasoline spark ignition engines, it has become necessary to incorporate a catalyst in the exhaust gas system to meet current emission control regulations in the European Union for passenger cars and light vehicles. Such catalysts are generally based on metal or ceramic honeycomb substrate structures as are well known for oxidation or three-way catalysts for gasoline-engined vehicles. During certain normal operations of diesel engines, particularly low speed and low temperature driving conditions such as city driving, the catalysts can become covered with carbonaceous material or soot. This may inhibit the gaseous reactions normally taking place on the catalyst surface by covering catalyst surfaces, and in worst cases may block partially or totally the channels in the honeycomb substrate, resulting in high pressure drop that can impair engine performance.

The deliberate trapping and subsequent combustion of soot is known in the context of heavy duty diesels (trucks and buses) in order to improve the environment, and we refer to our US Patent 4,902,487 which describes a system which has now been commercialised as the Continuously Regenerating Trap ("CRT"). This patent teaches a system involving a filter to remove soot, and combusting the soot using a gas containing NO₂. Such a gas is produced by fitting a catalyst upstream of the filter, to oxidise nitric oxide present in the exhaust gas to NO₂. Heavy duty diesels provide exhaust gases at relatively high temperature, and low sulphur fuel needs to be used.

We have now discovered that a variation on the concept of the CRT may be used to deal with soot inadvertently trapped on a catalyst in a light duty diesel. Light duty diesels operate at appreciably lower temperatures, especially under light load, than heavy duty diesels, which is generally a disadvantage for catalytic processes. It is also the case that the new generation direct injection gasoline engines can be limited in their engine management by avoidance of soot-forming conditions. It can increase the engine operating envelope, and possibly increase economy under certain conditions, if an emission control system which can deal with soot, can be developed.

The present invention provides an emission control system for internal combustion engines which emit carbonaceous particulates, particularly for diesel, especially light duty diesel, engines, said system comprising a first catalyst effective to oxidise NO to NO₂ and a second

catalyst, effective at least to oxidise HC, CO and VOF, each catalyst being supported on honeycomb flow-through monoliths, whereby soot particles trapped on or within said second catalyst monolith are combusted in the NO₂-containing gas from said first catalyst, and wherein the monolith used as a support for said first catalyst is such as to minimise the collection of soot particles.

Preferably, the first catalyst is formulated to have high activity for NO to NO₂ oxidation and is suitably a relatively high loading platinum catalyst. Such a catalyst may desirably have from about 50 to about 200g Pt/ft³ (1.77-7.06g Pt/litre of catalyst volume).

The monolithic support used for the first catalyst is preferably a metal monolith which desirably provides flexing and/or vibration of the honeycomb cell walls for the purpose of displacing any soot particles captured within the monolith. The monolith may be consciously designed to encourage such flexing and/or vibration, possibly using the natural vibration modes of the diesel engine.

Desirably, the monolith is significantly more open than the monoliths used for oxidation or three-way catalysts especially for gasoline engines, which are, for example desirably 400 cells/in² (62 cells/cm²) or higher, that is to say tend preferably to 600 cells/in² (93 cells/cm²). Such a monolith may be, for example, 100 or 200 cells/in² (15.5 or 31 cells/cm²). Desirably, the space velocity of gases flowing through the first catalyst is greater than that for the second catalyst, in order to reduce the opportunity for particulates to lodge therein.

The second catalyst may be a conventionally formulated diesel catalyst, for example on a monolith having 400 cells/in² or more. Soot formation from diesel engine exhausts has limited or excluded the use of the high cell density monoliths, which are desirable from a catalytic converter viewpoint. The second catalyst could also be a three-way catalyst, especially of the "lean-NOx" type, in which in addition to the oxidation reactions in respect of HC, NO and VOF, there is reduction of NOx to N₂, perhaps intermittently by the mechanism of NOx storage on components in the catalyst or by continuous regeneration of a selective catalyst.

The first and/or second catalysts may incorporate trapping components, either as discrete traps prior to the catalyst or as components of a layered or composite catalyst construction, to trap water vapour, sulphur, HC and/or NOx until they are released under catalyst operating conditions favourable to their conversion or use.

It is to be understood that the complex and varying gas compositions in an operating condition may not provide total conversion of NO to NO₂, but other oxidised nitrogen oxides may be produced. The necessary reaction is that such product NO₂ or oxidised nitrogen oxides contribute to the combustion of the soot particles, and, for ease of reference, the designation NO₂ is used herein. The practical requirement is that sufficient NO₂ is produced so that build-up of soot is limited to below the lev-

els at which problems arise. For this reason also, it may be desirable to have the first and second catalysts positioned close to each other, possibly within the same canister.

It is to be noted that some diesel fuels have high sulphur contents, eg above 500ppm, and we have found that the presence of sulphur compounds can inhibit the reaction forming NO₂ over a platinum catalyst. Desirably, therefore, low S fuel is used, but the inhibiting effect of sulphur may be reduced to some extent by using high catalyst or gas temperatures during periods in which gas and/or catalyst temperatures would normally be low, for example under light load conditions. This can be achieved by positioning the catalyst close to the engine. If necessary, supplementary electrical heating of at least the upstream face of the catalyst, optionally assisted by or replaced by infra-red or visible wavelength radiation from a suitable source, may be used to ensure combustion of the soot particles during those parts of the engine operating cycle at which the exhaust gas temperature and/or the catalyst temperature are below optimum. Certain other catalysts, eg zeolite-based catalysts, are not so sensitive as platinum-based catalysts to sulphur compound inhibition, and may be used if appropriate.

The present invention as described herein may be modified by the skilled person without departing from the inventive concepts.

Initial tests confirming the benefits of the present invention were carried out on a modified 1996 Audi 2.5TDI. A first catalyst which was a high loading (90g/cu ft = 3.1 8g/litre) platinum on a 4in x 4in metal honeycomb substrate of 200 cells/in² carrying a conventional oxide washcoat, was mounted upstream of the standard catalyst. Soot build-up under soot-forming conditions was reduced.

A further test was carried out by placing samples of standard diesel catalyst in the exhaust from a bench diesel engine for three hours. Visual inspection showed significant soot deposits. A 200 cells/in² (31 cells/cm²) metal honeycomb substrate carrying 70g/ft³ (= 2.47g/litre) Pt was placed in front of the sooted catalyst and the engine was run again. After a further three hours, the catalyst was recovered. Visual inspection showed that the soot deposits were partly removed.

Similar tests were carried out in which the visual difference was not very marked, but there was a weight reduction indicating soot combustion. Activity of the second catalyst was improved compared to the sooted catalyst.

The invention will now be described with reference to the accompanying drawings, in which:

Figure 1 is a schematic diagram of a catalyst system for a diesel engine according to the present invention,

Figure 2 is a chart showing NO₂ formation at different temperatures,

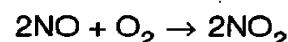
Figure 3 is a chart showing CO₂ formation at differ-

ent temperatures, and

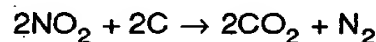
Figure 4 is a chart showing weights of soot collected on a second catalyst.

Referring to Figure 1, a single canister, 1, for fitting in the exhaust system of a light-duty diesel engine, encloses a first catalyst, 2. Said first catalyst is a 200 cells/in² (62 cells/cm²) metal substrate catalyst, carrying an alumina washcoat and 120g/ft³ (4.24g/litre) of Pt. There is a 1 cm gap between the first catalyst and a second catalyst which is a 400 cells/in² (124 cells/cm²) conventional commercial diesel oxidation catalyst. The first catalyst is half the length of the second catalyst, and this, together with the lower number of cells per unit area, means that the space velocity over the first catalyst is appreciably greater than over the second catalyst.

In operation, NO emitted from the diesel engine is converted over the first catalyst to NO₂, according to the equation



Over the second catalyst, NO₂ reacts with carbonaceous soot particles trapped on the face of the second catalyst or in the cells, according to the equation



A series of tests were carried out on a SCAT reactor (Simulated Car Activity Test) experimental rig. Samples of metal honeycomb catalyst substrate were washcoated with an alumina washcoat and loaded with different amounts of platinum by conventional impregnation technology, ranging from 70 to 150g/ft³ (2.47-5.30g/litre). The results are shown in Figure 2 as % of total NO_x converted to NO₂, plotted against temperature. Although, in general, the greater the Pt loading, the greater the conversion, the difference between the different Pt loadings was not dramatic.

The SCAT reactor rig was used again to test the effects of passing a synthetic exhaust gas comprising NO₂ over two samples of catalyst. One catalyst was as prepared, the other was a core cut from a catalyst which had been used in a diesel exhaust and therefore was sooted. CO₂ detected leaving the reactor is measured in ppm for both samples and is plotted in Figure 3 against catalyst temperature. It can readily be seen that the sooted catalyst generates appreciably more CO₂, indicating that the soot is being combusted.

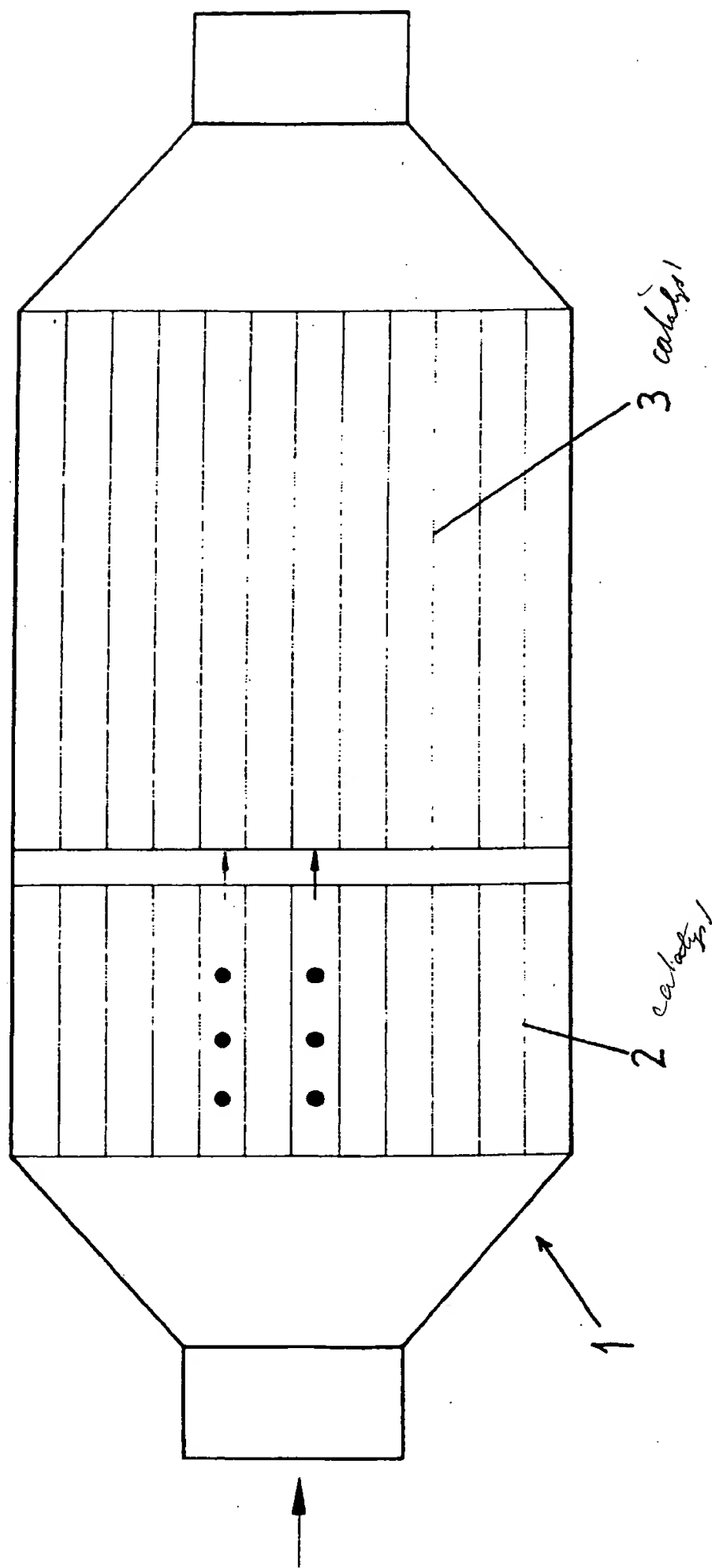
A further test was carried out using a Volvo diesel engine on a rest bench. The diesel exhaust gas was split into two parallel streams and passed through a sample conventional oxidation catalyst and an identical catalyst sample preceded by a first catalyst carrying 120g/ft³ (4.24g/litre) of Pt. The back pressure on each stream was equalised and the engine was run under conditions

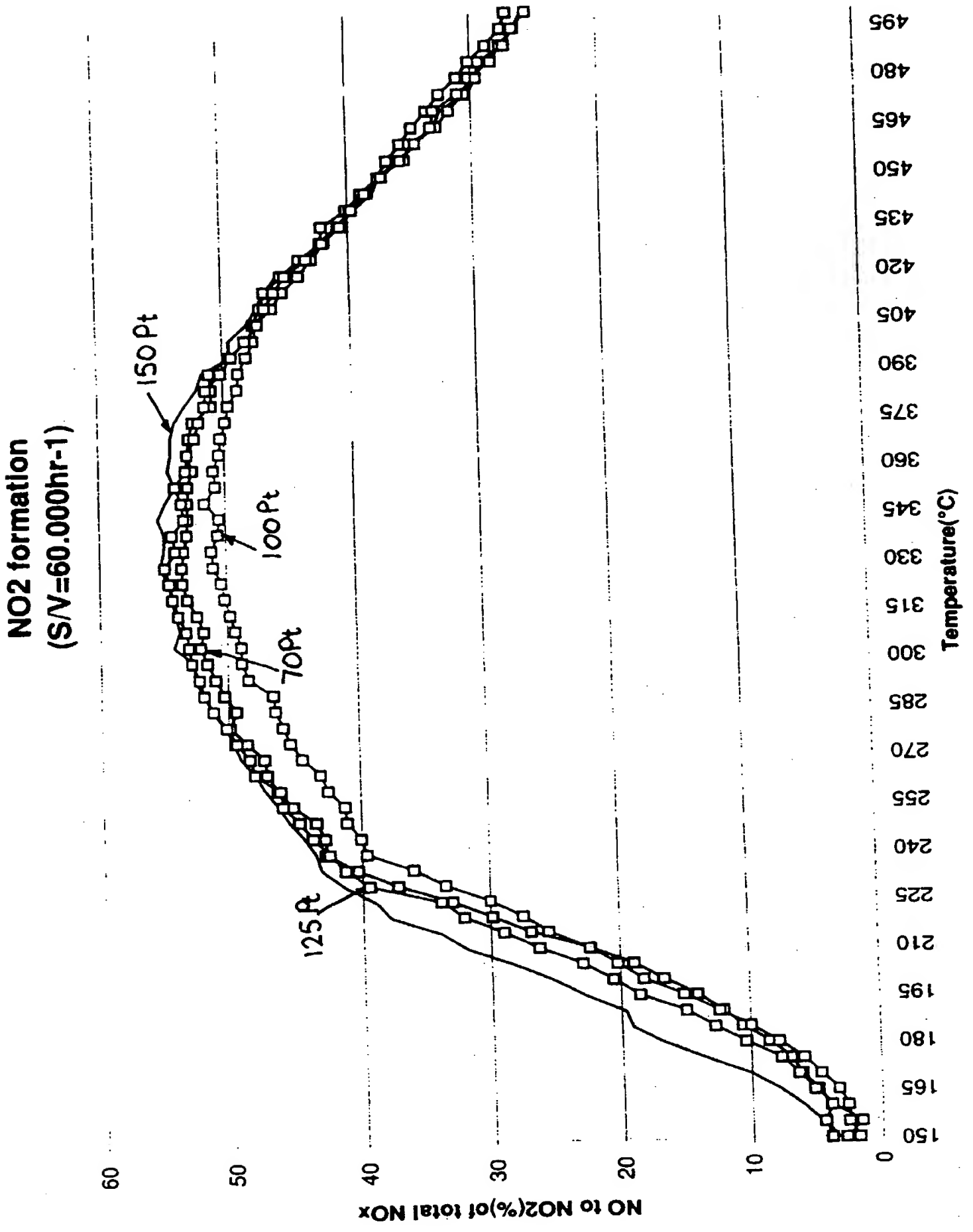
which were known to generate soot, for four hours. The fuel used in the engine contained 500ppm of sulphur. The oxidation catalysts were weighed before and after the test and the results are shown in Figure 4. The results are an average of three tests, and then the tests were repeated using a zero sulphur fuel. It can be seen that although the removal of sulphur from the diesel fuel reduces the amount of soot deposited on the catalyst, the effect of the first catalyst reduces the amount of soot by at least 50% by weight for sulphur-containing fuel and shows a greater improvement for sulphur-free fuel.

over an oxidation catalyst effective at least to oxidise HC, CO and VOF, the improvement comprising passing said gases over a first catalyst effective to oxidise NO to NO₂ and subsequently passing the gas enriched with NO₂ over said oxidation catalyst in order to cause combustion of soot particles trapped on or within said oxidation catalyst.

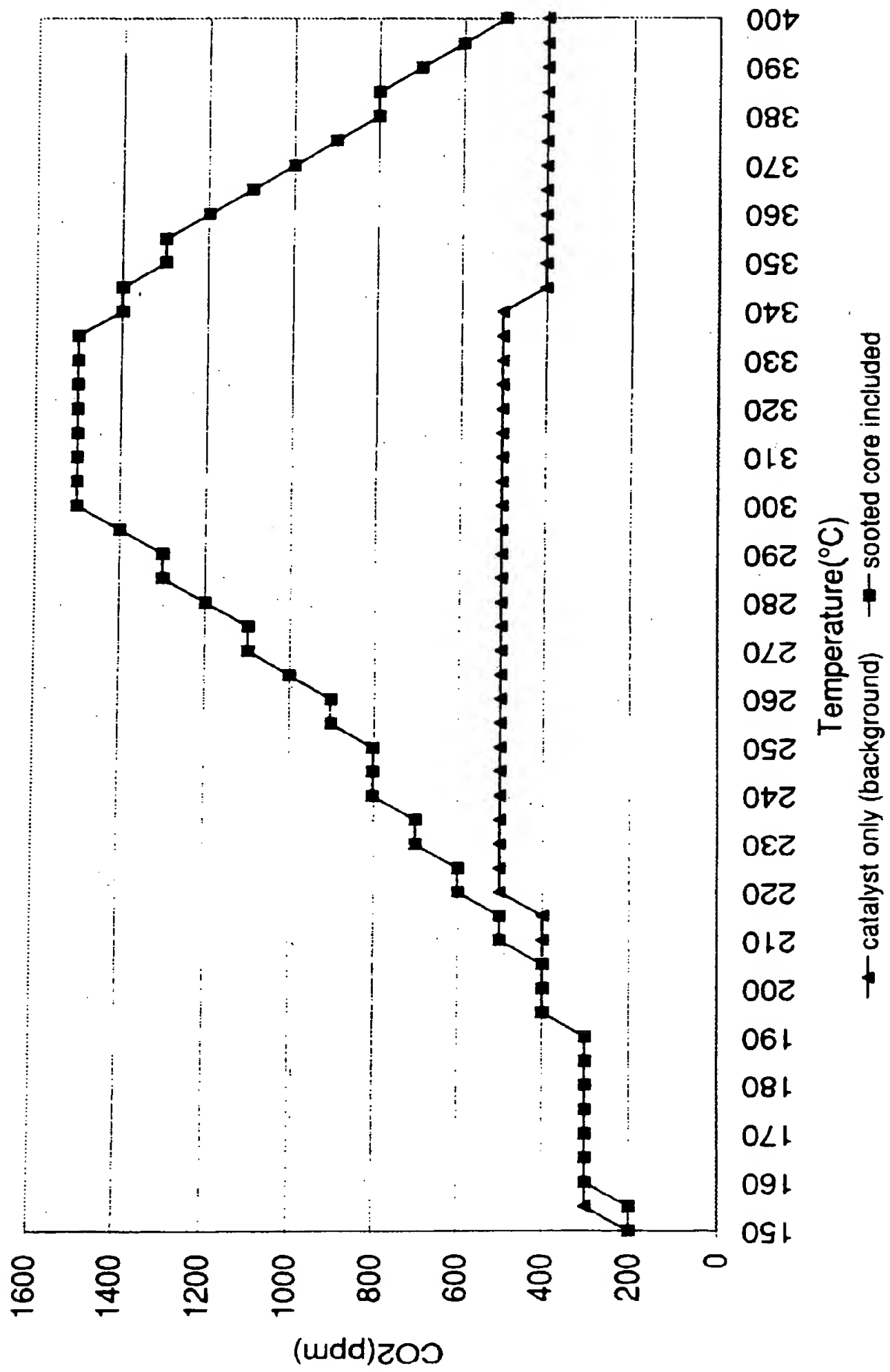
Claims

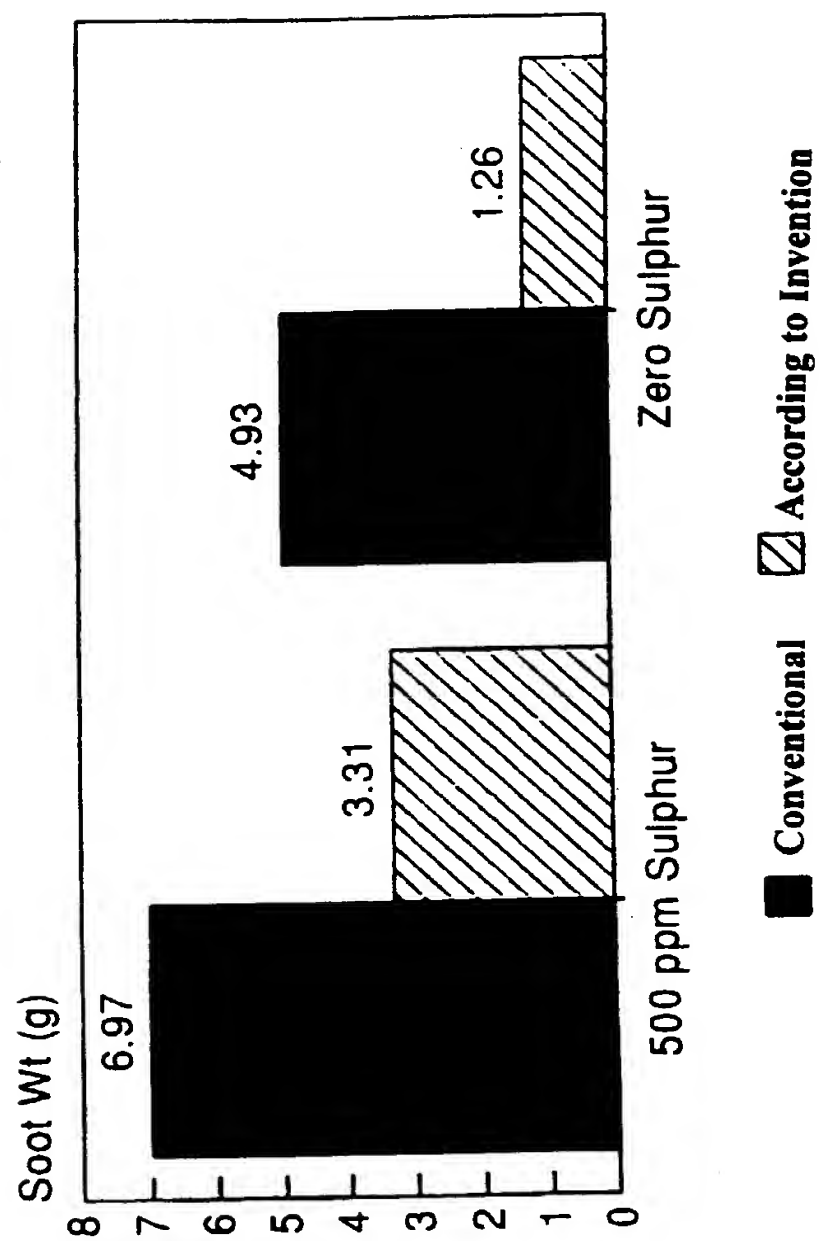
1. An emission control system for internal combustion engines which emit carbonaceous soot particles, comprising a first catalyst effective to oxidise NO to NO₂ and a second catalyst, effective at least to oxidise hydrocarbons, carbon monoxide and volatile organic fractions, each catalyst being supported on a honeycomb flow-through monolith, whereby soot particles trapped on or within said second catalyst monolith are combusted in the NO₂-containing gas from said first catalyst, and wherein the monolith used as a support for said first catalyst is such as to minimise the collection of soot particles.
2. A system according to claim 1, wherein said first catalyst contains platinum at a relatively high loading.
3. A system according to claim 2, wherein said first catalyst contains 1.77 to 7.06g/litre of catalyst volume, of platinum.
4. A system according to claim 1, 2 or 3, wherein said first catalyst has a metal honeycomb monolith support.
5. A system according to any of claims 1 to 4, wherein said first catalyst support has up to 31 cells/cm².
6. A system according to any of claim 1 to 5, wherein said second catalyst is selected from oxidation catalysts and lean-NO_x three-way catalysts.
7. An internal combustion engine which emits carbonaceous soot particles during at least part of the operating cycle, fitted with an emission control system according to any one of claims 1 to 6.
8. A light-duty diesel engine, fitted with an emission control system according to any one of claims 1 to 6.
9. In a process for the purification of exhaust gases from an internal combustion engine which emits carbonaceous soot particles by passing said gases





CO₂ formation after catalyst
(DF31/100Pt - S/V=30.000hr⁻¹)





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(88) Date of publication A3:
23.06.1999 Bulletin 1999/25

(51) Int Cl.⁶: **B01D 53/94**, F01N 3/20,
F01N 3/02

(43) Date of publication A2:
15.04.1998 Bulletin 1998/16

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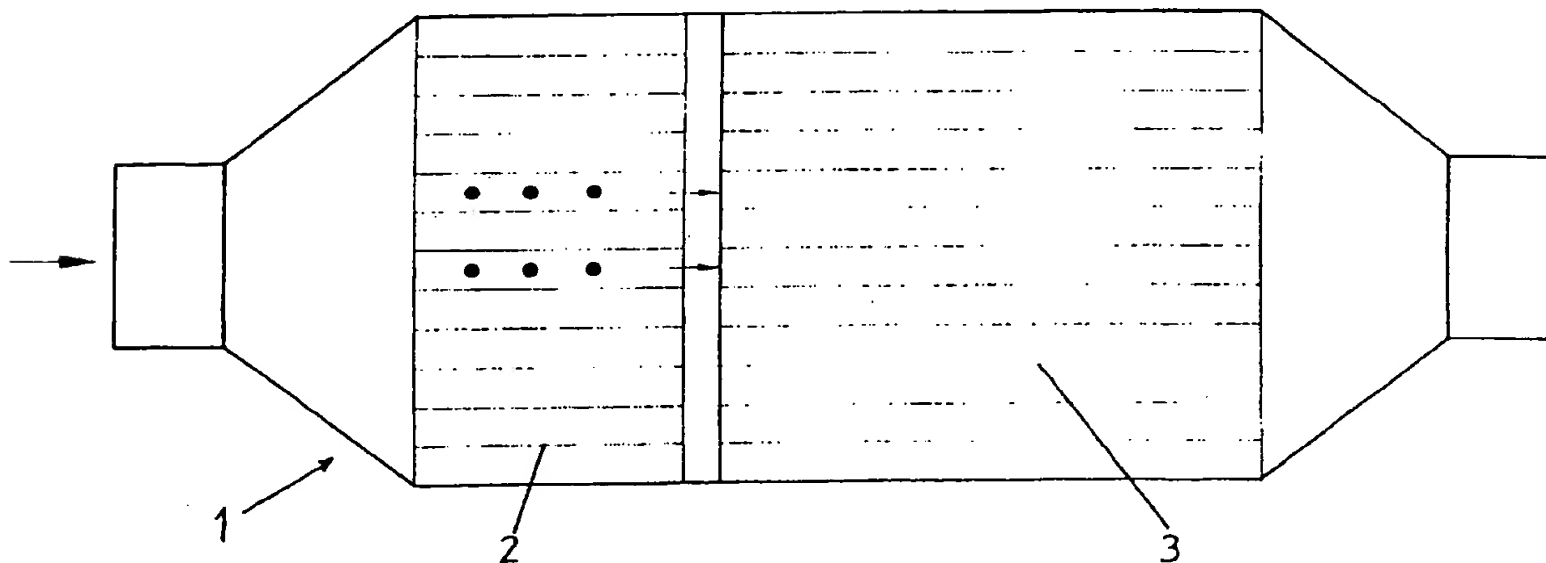
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EUROPEAN SEARCH REPORT

Application Number
EP 97 30 7691

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D,A	US 4 902 487 A (COOPER BARRY J ET AL) 20 February 1990 * column 1, line 44 - line 56 *	1,2	B01D53/94 F01N3/20 F01N3/02
A	DE 33 37 903 A (REIF GERHARD;BAUM WERNER) 9 May 1985 * figure 3 *	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			B01D F01N
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		29 April 1999	Faria, C
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

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ANNEX TO THE EUROPEAN SEARCH REPORT
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EP 97 30 7691

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29-04-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4902487 A	20-02-1990	AT 132940 T	15-01-1996
		DE 68925382 D	22-02-1996
		DE 68925382 T	15-05-1996
		DK 233389 A	14-11-1989
		EP 0341832 A	15-11-1989
		ES 2081301 T	01-03-1996
		GR 3018800 T	30-04-1996
		IE 71167 B	29-01-1997
		JP 1318715 A	25-12-1989
DE 3337903 A	09-05-1985	NONE	

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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